Mechanical Properties of Hydrophilicity Modified CaCO₃-Poly (Lactic Acid) Nanocomposite

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Abstract—The goal of this work is to modify surface of calcium carbonate nanoparticles with silica $(CaCO_3@SiO_2)$ via sol-gel process, and to investigate the influence of $CaCO_3@SiO_2$ on mechanical properties and fracture behavior of poly(lactic acid) nanocomposite. Modified $CaCO_3@SiO_2$ nanoparticles were prepared with different Si:Ca ratios. It is found that the Si/Ca wt% was increased with respect to the Si:Ca mole ratio used in the reaction. Incorporating $CaCO_3@SiO_2$ of 5 wt% increased elastic modulus, %elongation at break and notched impact strength of PLA nanocomposites. These properties of hydrophilic-modified $CaCO_3$ -poly(lactic acid) nanocomposite was increased with respect to the increasing of SiO_2 content on the surface of $CaCO_3$ nanoparticles. This implies that better compatibility between PLA matrix and nano-fillers was achieved after modification surface of $CaCO_3$ with SiO_2 layers.

Index Terms—Nanocomposite, poly(lactic acid), calcium carbonate nanoparticle, silica, sol-gel process.

I. INTRODUCTION

Poly(lactic acid) (PLA) or polylactide is a linear aliphatic biodegradable thermoplastic polyester, produced from renewable resources typically polymerized through the fermentation products of starch and sugar [1]. PLA plays an important role in various applications due to their biodegradable and biocompatible characters [1]-[5]. It offers a potential alternative to petrochemical plastics in many applications such as biomedical applications, controlled release films for fertilizers and waste-composting food package because of its high strength and stiffness with their biodegradable and biocompatible characters [2], [6], [7]. PLA, however, is comparatively brittle and stiff at room temperature [1], [8], so modification is needed for PLA in order to apply with flexible-desired applications such as food packaging.

Adding fillers into plastics are usually implemented not only confined to cost reduction, but also to control their physical and mechanical performance such as gas barrier properties, thermal stability, strength, melt viscosity and biodegradation rate [1], [4], [5], [9], [10].

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Recently, there are widely improving of polymer properties using nano-size inorganic fillers such as ZnO, SiO₂, clay, precipitated calcium carbonate (PCC), and noble metals [11], [12]. Nano-reinforcements of biodegradable polymers have strong promises in designing eco-friendly green nanocomposites for several applications. A fairly new area of composites has emerged in which the reinforcing materials have the dimensions in nanometric scale. These composites are significant due to their nano-scale dispersion, even with very low level of nano-filler incorporation (<5 wt%) which results in high surface area [5]. Properties of filler-filled composites are closely related to the dispersion of the particles in polymer matrix.

In consideration of various fillers, calcium carbonate (CaCO₃) is the famous material, widely used in various industries, due to its high amount of loading in plastics and low cost [13], [14]. The reinforcing effect of CaCO₃ particles has been studied in polymer systems such as high density polyethylene (HDPE) [15], nylon [16], polypropylene (PP) [17], polyketone[18], acrylonitrile butadiene styrene (ABS) [19], and thermoplastic polyurethane (TPU) [20]. The mechanical properties were found to be significantly improved by the addition of fine CaCO₃ particles [15]-[20]. Large scale plastic deformation was found to be initiated by interfacial debonding and the subsequent relaxation of triaxial tensile stress [21]. Since PLA is well known for its difficulty to crystalline, adding CaCO₃ could have an impact on its properties as well as potential applications replacing petrochemical based plastics [14], [22].

In order to produce CaCO₃@SiO₂.nH₂O nanocomposite particles, CaCO₃ was used as a template nucleus and the surface of nucleus was encapsulated by a SiO₂.nH₂O nanolayer. Synthetic silica fixed on the surfaces of calcium carbonate particles has good properties such as a high specific surface area and high absorbability, benefits to form linkage at the interface of two materials (plastic and filler), connecting to improve mechanical properties of materials [23], [24].

Therefore, this work aims to modify surface of calcium carbonate nanoparticles with silica $(CaCO_3@SiO_2)$ via sol-gel process, and to investigate the influence of $CaCO_3@SiO_2$ on mechanical properties and fracture behavior of poly(lactic acid) nanocomposite.

II. EXPERIMENTAL

A. Materials

Poly(lactic acid) (PLA, 2002D, NatureWorks LLC) and calcium carbonate (CaCO₃, NPCC 101, Behn Meyer Chemical) were dried overnight at 60 °C in order to remove structural water before they were brought into the compounding process.

In the preparation of $CaCO_3@SiO_2$ particles via sol-gel process, tetraethylorthosilicate (TEOS, Fluka), ethanol and ammonium hydroxide (NH₄OH, 35%NH₃, Mallinckrodt Chemical) were used.

B. Preparation of Silica Coated Calcium Carbonate Composite Particles

The Hydrophilic SiO₂ Surface Modified CaCO₃ $(CaCO_3@SiO_2.nH_2O)$ particles were prepared by hydrolysis-condensation polymerization of TEOS on the surface of CaCO₃ particles. The CaCO₃ particles were dispersed into the mixture of TEOS, 200 ml ethanol, and 300 ml distillation water. The mole ratios of TEOS to CaCO₃ were vary as 1:30, 1:20 and 1:10, then 100 ml NH₄OH was added slowly, and the mixture was vigorously stirred at 40 °C for 6 h. After the reaction, the $CaCO_3(a)SiO_2$ particles were filtrated and washed with ethanol followed by distillation water for several times to remove dissociative polysiloxane, unreacted monomer, and polysiloxane oligomers. The CaCO₃@SiO₂ particles were then dried at 60°C in oven.

C. Particle Characterization

The characteristic of the CaCO₃@SiO₂ particles was characterized by Fourier transform infrared (FT-IR, Bruker vector-22). The morphology of CaCO₃@SiO₂ particles were investigated using transmission electron microscopy (TEM, Jeol model JEM-1230). The elemental content of CaCO₃@SiO₂ particle was analyzed by X-ray fluorescence spectrometer (XRF, Phillips PW-2404).

D. Preparation of PLA Nanocomposites

Prior to compounding, PLA, CaCO₃ and CaCO3@SiO₂ were dried overnight at 60 °C in order to remove residual moisture. En Mach SHJ-25 co-rotating twin-screw extruder was used to compound the 5 wt% content of CaCO₃ and CaCO₃@SiO₂-PLA nanocomposites. The barrel temperature profile adopted during blending was ranged from 150 °C in the feed zone to 170 °C in metering zone at the fixed screw speed of 130 rpm. Then, the extruded materials were compression molded into standard tensile and impact specimens using LabTech Compression Molding machine with mold temperature of 170 °C and mold pressure of 20,000 psi for 5 min.

E. Mechanical Analysis

Tensile test was carried out in according to ASTM D638 type V using a universal testing machine (Instron 5969) under ambient conditions with crosshead speeds of 10 mm/min. Notched Izod impact test, according to ASTM D256, was done on notched impact specimens, by using an instrument impact tester (Zwick model B5102.202 Izod Pendulum 4 J)

In order to study the compatibility of PLA and fillers, glass transition temperature (T_g) and crystallization temperature (T_c) of PLA and PLA nanocomposites were studied by differential scanning calorimeter (DSC, Mettler Toledo DSC822e) under nitrogen atmosphere. The temperature was raised from -20 to 180 °C with the heating ramp of 10 °C/min.

F. Morphological Studied

Morphology of nanocomposite was investigated by scanning electron microscopy (SEM) using Hitachi Model S3400N instrument. Prior to testing, the fracture surfaces of samples were sputtered with platinum.

III. RESULTS AND DISCUSSION

A. Characterization of Modified CaCO₃ Nanoparticle

Infrared spectra of CaCO₃ and CaCO₃@SiO₂ were presented in Fig. 1. The FT-IR absorption peaks of CaCO₃ and CaCO₃@SiO₂ displayed the absorption peak of crystal at about 875 cm⁻¹ and 710 cm⁻¹. The absorption peak at 875 cm⁻¹ indicated the CO₃²⁻ out-of-plane deformation mode of the aragonite while the absorption peak of 710 cm⁻¹ showed the calcite formed [25]. It shows that the product was the mixture of calcite and aragonite. In addition there were interesting absorption peak at about 1,780 cm⁻¹, 2,950-2,850 cm⁻¹ and the broad about 3,600-3,200 cm⁻¹. These peaks indicated C=O stretching in carboxylic acid, alkyl C-H stretching and O-H stretching, respectively. The absorption proved that all types of CaCO₃ were surface treated by some fatty acid for preventing the re-agglomeration of particles.

The hydrolysis of TEOS would be occurred in the presence of water and alkaline catalysts, and Si(OH)₄ was formed as one of the of hydrolysates (scheme 1). The adding of NH₄OH was to promote the hydrolysis of TEOS. Then, Si(OH)₄ molecule would polymerize with other Si(OH)₄ or TEOS molecule (scheme 2 or scheme 3). The product of this step was the monomer or oligomers of polysiloxane. Finally, the monomers or oligomers of polysiloxane continue to polymerize and form a film of high relative molecular mass polysiloxane with a three-dimensional network structure (scheme 4). Because water and TEOS are immiscible, a mutual solvent such as ethanol is normally used as a homogenizing agent. Fine particles CaCO₃ can provide nucleation centers and decrease the kinetic barrier to nucleation of hydrophilic silica. Furthermore, the monomers or oligomers of polysiloxane along with Si(OH)₄ molecules have very high activities, so they can be adsorbed to the surface of CaCO₃ rapidly. The polymerization of silica (scheme 4) occurs on the surface of the CaCO₃ particles and the silica film thus covers around the CaCO₃ particles tightly.

$$\begin{split} & \text{Si}(\text{OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + 4\text{C}_2\text{H}_5\text{OH} \quad \text{scheme 1} \\ & \text{Si}(\text{OH})_4 + \text{Si}(\text{OH})_4 \quad \rightarrow (\text{HO})_3\text{Si} - \text{O} - \text{Si}(\text{OH})_3 + \text{H}_2\text{O} \\ & \text{Si}(\text{OH})_4 + \text{Si}(\text{C}_2\text{H}_5\text{O})_4 \rightarrow (\text{HO})_3\text{Si} - \text{O} - \text{Si}(\text{C}_2\text{H}_5)_3 + \text{C}_2\text{H}_5\text{OH} \\ & \text{x}(\text{Si} - \text{O} - \text{Si}) \rightarrow (\text{Si} - \text{O} - \text{Si})x \quad \text{scheme 4} \end{split}$$



Fig. 1. FT-IR spectra of (a) CaCO₃ nanoparticle and (b) CaCO₃@SiO₂ nanoparticle.

The infrared spectra of the particles from FT-IR characterization were analyzed in the range of 400 cm⁻¹ to 4,000 cm⁻¹ as shown in Fig. 1. It can be seen that the spectrum of blank CaCO₃ nanoparticles is quite the same as the spectrum of CaCO₃@SiO₂ but there was transmitting bands at about 1,100 cm⁻¹ of Si—O—Si asymmetric stretching [27] of CaCO₃@SiO₂ nanoparticles. This revealed that the SiO₂ was occurred in the reaction proved the successful of the development of CaCO₃@SiO₂ nanoparticles.





Fig. 2. Morphologies of (a) CaCO₃ nanoparticles and (b-c) CaCO₃@SiO₂ nanoparticles (magnificent 200,000x).

In addition, morphologies of CaCO₃ nanoparticles and CaCO₃@SiO₂ nanoparticles were shown as TEM images in Fig. 2. It can be seen that there were SiO₂ layers coated around the CaCO₃ nanoparticles causing the slightly increase in particle sizes, however, the particle size of CaCO₃@SiO₂ particles were still in the range of nano-scale. Layers of synthesized SiO₂ were coated on the surface of CaCO₃ nanoparticles. However, some crystals of synthesized SiO₂ grew stacked to each other. The elemental content of CaCO₃@SiO₂ as shown in Table I was analyzed by XRF, which the Si/Ca wt% in CaCO₃@SiO₂ particles was increased with respect to the Si:Ca mole ratio used in the reaction.

TABLE I: THE ELEMENTAL ANALYSIS OF CaCO3 @SiO2 NANOPARTICLES

	Concentration (%wt)		
Element	CaCO ₃ @SiO ₂ (30:1)	CaCO ₃ @SiO ₂ (20:1)	CaCO ₃ @SiO ₂ (10:1)
0	58.72	53.83	50.83
Na	0.02	0.04	0.07
Mg	0.13	0.16	0.13
Al	0.04	0.05	0.07
Si	0.87	1.92	3.91
Р	N/D	N/D	N/D
S	0.02	0.02	0.01
Cl	N/D	N/D	N/D
K	N/D	N/D	N/D
Ca	40.11	43.89	44.9
Fe	0.05	0.05	0.04
Sr	0.04	0.04	0.04
Total	100	100	100

TABLE II: COMPARISON OF Si/Ca ratio in CaCO₃@SiO₂

Particles (mole ratio)	Si/Ca (%wt), XRF
CaCO ₃ @SiO ₂ (30:1)	2.17
CaCO ₃ @SiO ₂ (20:1)	4.37
CaCO ₃ @SiO ₂ (10:1)	8.71

B. Mechanical Analysis

Fig. 3 shows tensile properties of PLA-CaCO₃ and PLA-CaCO₃@SiO₂ nanocomposites. Young's moduli of PLA and PLA nanocomposites are illustrated in Fig. 3(a). Compared with neat PLA, incorporating CaCO₃ nanoparticles of 5 wt% relatively did not improve elastic modulus of PLA nanocomposite. It indicates that CaCO₃ nanoparticles did not have good efficiency to reinforce nanocomposite as well as those added nanoclays. Lack of reinforcing ability of CaCO₃ nanoparticles would come from their cubic shape that did not good for load bearing compared to the platelets in nanoclays. Moreover, the fatty acid based sizing agents, treated on CaCO₃ surface to prevent them from agglomeration, would cause lubricating effect in the nanocomposites during the load bearing [27]. In the other

hand, incorporating $CaCO_3@SiO_2$ with the same content did increase elastic modulus of PLA nanocomposites, and elastic modulus of PLA-CaCO_3@SiO_2 nanocomposite increased with respect to increasing of SiO_2 content on the surface of CaCO_3 nanoparticles.

In this work, compatibility between PLA matrix and CaCO₃ nanoparticles was not modified by means of coupling agents. In the presence of nano-fillers, the decrease of %elongation at break of PLA nanocomposite in Fig. 3(b) demonstrates that the interfacial interaction between PLA matrix and CaCO₃ was so poor that fillers induced a definite decrease in elongation [15], because they acted as stress concentrator to promote crack initiation. Surprisingly, the increase of SiO₂ content on CaCO₃@SiO₂ retarded crack propagation to occur at higher % elongation at break. This implies that better compatibility between polymer matrix and filler was achieved. This was due to good interaction between SiO₂ coated around the CaCO₃ and the hydroxyl groups at the chain ends in PLA matrix. And, this is also possibly the reason how the elastic modulus of PLA-CaCO₃@SiO₂ nanocomposite was improved.

The compatibility of PLA and PLA-CaCO₃@SiO₂ was studied by means of thermal properties (Tg and Tc) from DSC test. Addition of CaCO3 did not affect Tg of PLA in the same fashion of CaCO3@SiO2 did as seen in Table III. This confirms no interaction between CaCO3 and PLA molecules. Meanwhile, more energy is required for PLA molecules to vibrate when they were surrounded with CaCO₃@SiO₂. It is observed that T_c of PLA and its nanocomposite appeared in the heating scan rather than in the cooling scan. T_c of PLA decreased with respect to SiO₂ contents on CaCO₃ surface. This implies the synergism between polymer matrix and filler on PLA crystallization [28]. Since the CaCO₃@SiO₂ particles were dispersed well in PLA matrix, the relatively higher hydrophillic SiO₂ coated layers acted like the nucleating sites for PLA molecules to crystalline so that the crystallization of PLA occurred at lower T_c than those CaCO₃ without SiO₂ coating.

TABLE III: Tg AND Tc of PLA-CaCO₃@SiO₂ NANOCOMPOSITE

Particles (mole ratio)	T _g (°C)	T_{c} (°C)
PLA-CaCO ₃	51.98	123.70
PLA-CaCO ₃ @SiO ₂ (30:1)	52.22	123.53
PLA-CaCO ₃ @SiO ₂ (20:1)	52.38	120.18
PLA-CaCO ₃ @SiO ₂ (10:1)	52.34	117.43





Fig. 3. Tensile properties of PLA nanocomposites: (a) Young's modulus and (b) %Elongation at break.



Fig. 4. Impact strength of PLA nanocomposites.

Fig. 4 presents the notched impact strength of PLA-CaCO₃ and PLA-CaCO₃@SiO₂ nanocomposites. Similarly to tensile test, the presence of CaCO₃ nanoparticles became the stress concentration in the PLA matrix causing them to premature breakage. Adding CaCO₃@SiO₂ nanoparticles showed the improvement in impact resistance of PLA. Impact strength of PLA was increased with the increasing content of SiO₂ on the surface of CaCO₃ particles. The incorporation of CaCO₃@SiO₂ nanoparticles with Si/Ca wt% in PLA more than 2 wt% could improve impact strength of PLA. This means that modification the surface of CaCO₃ nanoparticles with small amount of SiO₂ via sol-gel process could provide better compatible with PLA matrix and CaCO₃ nanoparticle yielding more desired mechanical properties.

C. Morphology of PLA Nanocompsoite

SEM micrographs in Fig. 4 reveal the fracture behavior of PLA-CaCO₃ and PLA-CaCO₃@SiO₂ neat PLA. nanocomposites. Fracture surface of neat PLA was smooth with local ductile breaking as craze and crack propagation occurred during the impact loading. When CaCO₃ was added into PLA matrix, they became stress concentrators promoting crack initiation, thus local ductile breaking diminished causing decrease in impact strength. Fracture surface of PLA-CaCO₃@SiO₂ nanocomposites looked smooth similarly to that of neat PLA. However, it presented finer local ductile breaking indicating crack initiation occurred at the CaCO₃ nanoparticles but crack propagation occurred with higher extension.









Fig. 4. SEM micrographs of impact fracture surface of neat PLA and PLA nanocomposites : (a) PLA, (b) PLA-CaCO₃, and (c) PLA-CaCO₃@SiO₂.

IV. CONCLUSION

In this study, modified CaCO₃@SiO₂ nanoparticles were prepared with different Si/Ca ratios. SiO₂ layers coated around the CaCO₃ nanoparticles causing the slightly increase in particle sizes, however, the particle size of CaCO₃@SiO₂ particles were still in the range of nano-scale. It is found that the Si/Ca wt% was increased with respect to the Si:Ca mole ratio used in the reaction. Compared to PLA-CaCO₃ nanocomposite, incorporating CaCO₃@SiO₂ at the same content increased elastic modulus, %elongation at break and notched impact strength of PLA nanocomposites, which these properties of PLA-CaCO₃@SiO₂ nanocomposite was increased with respect to the increasing of SiO₂ content on the surface of CaCO₃ nanoparticles. This implies that better compatibility between polymer matrix and filler was achieved after modification surface of CaCO₃ with SiO₂.

REFERENCES

- L.-T. Lim, R. Auras, and M. Rubino, "Processing technologies for poly(lactic acid)," Prog. Polym. Sci., Vol. 33, pp. 820-852, Aug. 2008.
- [2] F.P.L. Mantia and M. Morreale, "Green composites: A brief review," Composites Part A Vol. 42, pp. 579-588, Jun. 2011.
- [3] D. Garlotta, "A Literature Review of Poly(Lactic Acid)," J. Polym. Environ., Vol. 9, pp. 63-84, Apr.2001.
- [4] T.D. Lam, T.V. Hoang, D.T. Quang, and J.S. Kim, "Effect of nanosized and surface-modified precipitated calcium carbonate on properties of CaCO₃/polypropylene nanocomposites," Mater. Sci. Eng., A, Vol.501, pp. 87-93, Feb. 2009.
- [5] S.S. Ray and M. Bousmina, "Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world," Prog. Mater. Sci., Vol. 50, pp. 962-1079 Nov. 2005.
- [6] B.-K. Chen, C.-H. Shen, S.-C. Chen and A. F. Chen, "Ductile PLA modified with methacryloyloxyalkylisocyanate improves mechanical properties," Polymer, Vol. 51, pp. 4667-4672, Oct. 2010.
- [7] V. Siracusa, P. Rocculi, S. Romani, and M.D. Rosa, "Biodegradable polymers for food packaging: a review," Trends in Food Science & Technology, Vol. 19, pp. 634-643, Dec. 2008.
- [8] M.-A. Paul, M. Alexandre, P. Degée, C. Henrist, A. Rulmont, and P. Dubois, "New nanocomposite materials based on plasticized poly(l-lactide) and organo-modified montmorillonites: thermal and morphological study," Polymer, Vol. 44, pp. 443-450, Jan. 2003.
 [9] R. Dangtungee and P. Supaphol, "Melt rheology and extrudate swell of
- [9] R. Dangtungee and P. Supaphol, "Melt rheology and extrudate swell of titanium (IV) oxide nanoparticle-filled isotactic polypropylene: Effects of content and surface characteristics," Polymer Testing, Vol. 27, pp. 951-956, Dec. 2008.
- [10] A. Sorrentino, G. Gorrasi, and V. Vittoria, "Potential perspectives of bio-nanocomposites for food packaging applications," Trends in Food Science & Technology, Vol. 18, pp. 84-95, Feb. 2007.
- [11] I. Pluta, M. Murariu, M. Alexandre, A. Galeski, and P. Dubois, "Polylactide compositions. The influence of ageing on the structure, thermal and viscoelastic properties of PLA/calcium sulfate composites," Polym. Degrad. Stab., Vol. 93, pp. 925-931, May 2008.
 [12] C. Thellen, C. Orroth, D. Froio, D. Ziegler, J. Lucciarini, R. Farrell,
- [12] C. Thellen, C. Orroth, D. Froio, D. Ziegler, J. Lucciarini, R. Farrell, N.A. D'Souza, and J.A. Ratto, "Influence of montmorillonite layered silicate on plasticized poly(l-lactide) blown films," Polymer, Vol. 46, pp. 11716-11727, Nov. 2005.
- [13] S. Zhang and X. Li, "Synthesis and characterization of CaCO₃@SiO₂ core-shell nanoparticles," Powder Technology, Vol. 141, pp. 75-79, Mar. 2004.
- [14] S. Miao, "Investigation on NIR, coating mechanism of PS-b-PAA coated calcium carbonate particulate," Appl. Surf. Sci., Vol. 220, pp. 298-303, Dec. 2003.
- [15] Z. Bartczak, A.S. Argon, R.E. Cohen, and M. Weinberg, "Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles," Polymer, Vol. 40, pp. 2347-2365, Apr. 1999.
- [16] M.W.L. Wilbrink, A.S. Argon, R.E. Cohen, and M. Weinberg, "Toughenability of Nylon-6 with CaCO₃ filler particles: new findings and general principles," Polymer, Vol. 42, Dec. 2001. pp.10155-10180, Dec. 2001.
- [17] W.C.J. Zuiderduin, C. Westzaan, J. Huétink, and R.J. Gaymans, "Toughening of polypropylene with calcium carbonate particles," Polymer, Vol. 44, pp. 261-275, Jan. 2003.
- [18] W.C.J. Zuiderduin, J. Huétink, and R.J. Gaymans, "Rigid particle toughening of aliphatic polyketone," Polymer, Vol. 47, pp. 5880-5887, Jul. 2006.
- [19] L. Jiang, Y.C. Lam, K.C. Tam, T.H. Chua, G.W. Sim, and L.S. Ang, "Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate," Polymer, Vol. 46, pp. 243-252, Jan. 2005.
- [20] L. Jiang, Y.C. Lam, K.C. Tam, D.T. Li, and J. Zhang, "The influence of fatty acid coating on the rheological and mechanical properties of thermoplastic polyurethane (TPU)/nano-sized precipitated calcium carbonate (NPCC) composites," Polymer Bulletin, Vol. 57, pp. 575-586, May 2006.
- [21] L. Jiang, J. Zhang, and M.P. Wolcott, "Comparison of polylactide/ nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms," Polymer, Vol. 48, pp. 7632-7644, Dec. 2007.
- [22] K. Gorna, M. Hund, M. Vuc ak, F. Gröhn, and G. Wegner, "Amorphous calcium carbonate in form of spherical nanosized particles and its application as fillers for polymers," Mater. Sci. Eng., A, Vol. 477, pp. 217-225, Mar. 2008.

hollow-structures nanomaterials and synthesizing method," U.S. Patent 170 178, Aug. 4, 2005.

- [24] K. Tanabe and K. Mitsuhashi, "Silica-calcium carbonate composite particles," U.S. Patent 7 060 127 Jun. 13, 2006.
- [25] C.-L. Yao, C.-X. Qi, J.-M. Zhu, and W.-H. Xu, "Unusual morphology of calciumcarbonate controlled by amino acids in agarose gel," J. Chil. Chem. Soc., Vol. 55, pp. 270-273, Jun. 2010.
- [26] Z.-P. Cheng, Y. Yang, F.-S. Li, and Z. –H. Pan, "Synthesis and characterization of aluminum particles coated with uniform silica shell," Trans. Nonferrous Met. Soc. China Vol. 18, pp. 378-382, Apr. 2008.
- [27] S. Yan, J. Yin, J. Yang and X. Chen, "Structural characteristics and thermal properties of plasticized poly(l-lactide)-silica nanocomposites synthesized by sol-gel method," Mater. Lett., Vol. 61, pp. 2683-2686, May 2007.
- [28] H.T. Lim, H. Liu, K. H. Ahn, S. J. Lee, and J. S. Hong, "Effect of added ionomer on morphology and properties of PP/organoclay nanocomposites," Korean J. Chem. Eng., Vol. 27, pp. 705-715, 2010.



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